UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2008/2009

June 2009

KOT 222 – Organic Chemistry II
[Kimia Organik II]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **SEVENTEEN** printed pages before you begin the examination.

Instructions:

Answer any **FIVE** (5) questions.

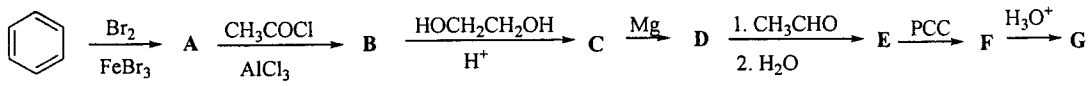
You may answer the question either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

Appendix: Spectroscopy Table.

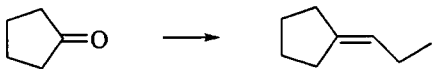
...2/-

1. (a) Identify **A** – **G** in the reaction sequence below. When a mixture of *ortho* and *para* products results in electrophilic aromatic substitution, consider the *para* product only. Sketch the ^{1}H NMR spectrum of **G**.



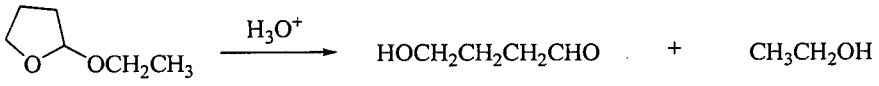
(10 marks)

(b) Show two different methods for carrying out the following transformation: a one-step method using a Wittig reagent, and a two-step method using a Grignard reagent. Which one, if any, is preferred?



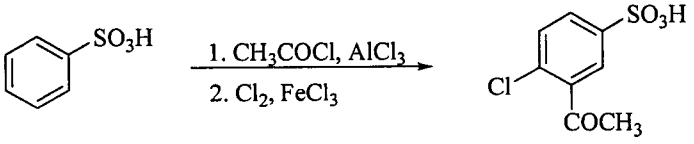
(6 marks)

(c) Write a stepwise mechanism for the following reaction:



(4 marks)

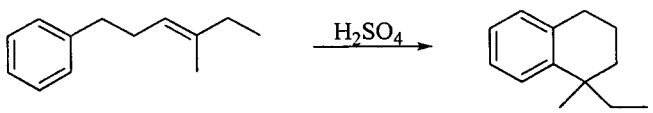
2. (a) Explain why the following reaction will not give the product **H**. Suggest a synthesis of **H** from benzene.



(**H**)

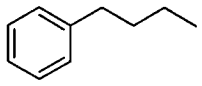
(6 marks)

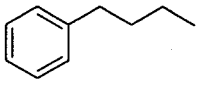
(b) Draw a stepwise mechanism for the following reaction:

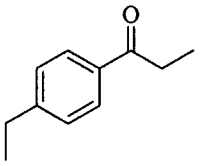


(5 marks)

(c) Predict the products of the following reactions:

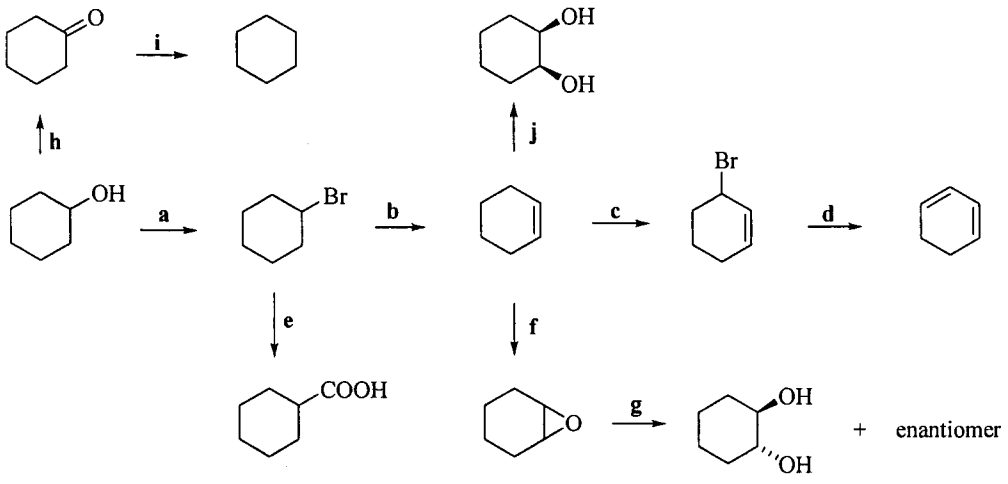
(i)  $\xrightarrow[hv]{Br_2}$

(ii)  $\xrightarrow[FeBr_3]{Br_2}$

(iii)  $\xrightarrow{Zn\ (Hg),\ HCl}$

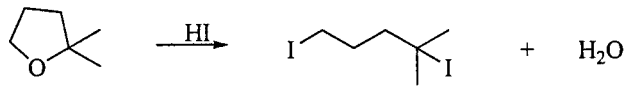
(9 marks)

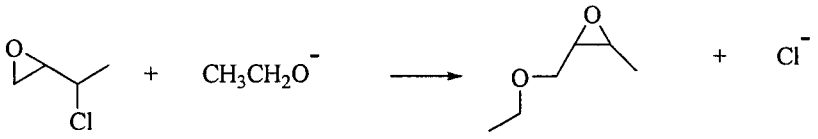
3. (a) Identify the reagents **a-j** needed to carry out each reaction.



(10 marks)

(b) Draw a stepwise mechanism for each of the following reactions:

(i) 

(ii) 

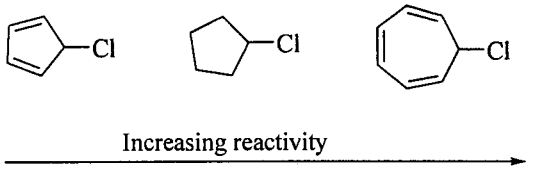
(10 marks)

4. (a) Use the polygon rule to show why the cation (**1**) is aromatic.

(**1**)

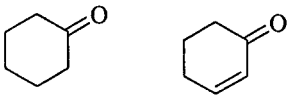
(6 marks)

(b) Explain the observed rate of reactivity of the following 2° alkyl halides in an S_N1 reaction.



(8 marks)

(c) Explain why a carbonyl absorption shifts to lower frequency in an α, β-unsaturated carbonyl compound. For example, the carbonyl absorption occurs at 1720 cm^{-1} for cyclohexanone (**2**), and at 1685 cm^{-1} for 2-cyclohexenone (**3**).



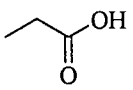
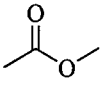
(**2**) (**3**)

(6 marks)

5. (a) How would each of the following pairs of compounds differ in their IR spectra?

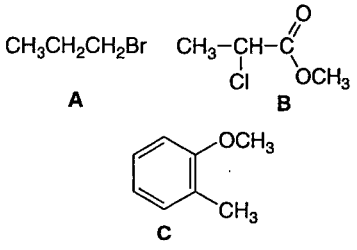
(i)  and $HC{\equiv}CCH_2CH_2CH_3$

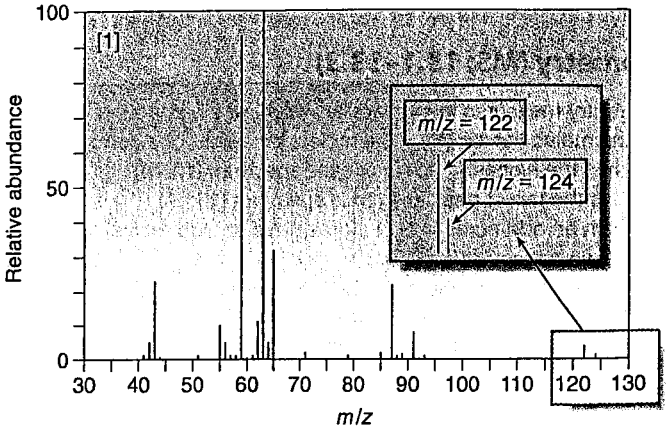
(ii) $HC{\equiv}CCH_2N(CH_2CH_3)_2$ and $CH_3(CH_2)_5C{\equiv}N$

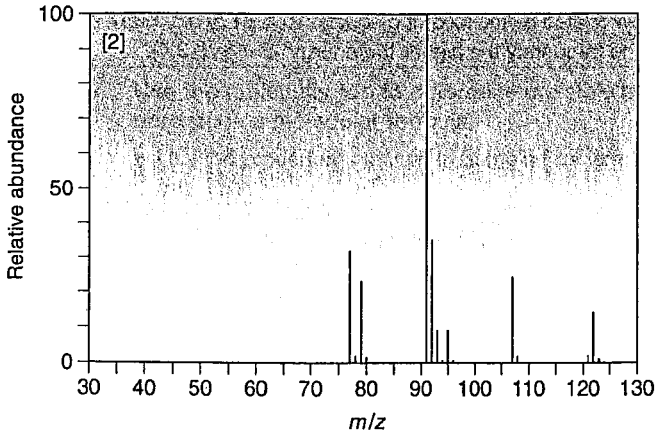
(iii)  and 

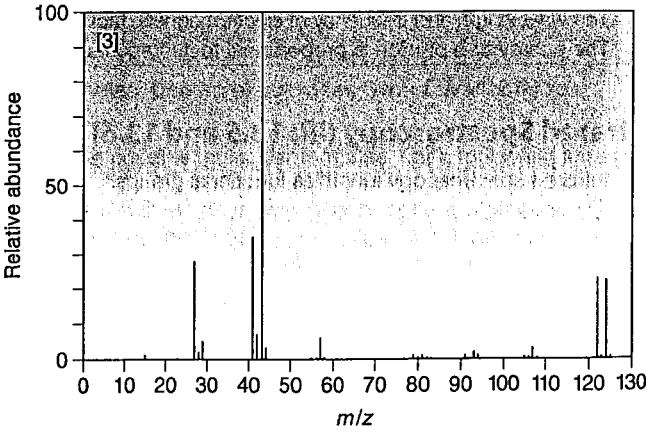
(10 marks)

(b) The mass spectra of **A**, **B**, and **C** are shown below. Match each structure to its mass spectrum.



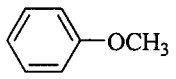
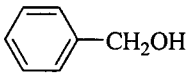


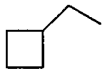




(10 marks)

6. (a) How would each pair of compounds be different in their ^{1}H NMR spectra?

(i)  and 

(ii)  and 

(6 marks)

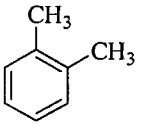
(b) Identify the structures of isomers **I** and **J**. Their molecular formula is $C_9H_{10}O$.

Compound **I**: IR absorption at 1742 cm^{-1}; ^{1}H NMR (ppm): 2.15 (singlet, 3 H), 3.70 (singlet, 3 H), 7.20 (broad singlet, 5 H).

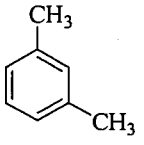
Compound **J**: IR absorption at 1688 cm^{-1}; ^{1}H NMR (ppm): 1.22 (triplet, 3 H), 2.98 (quartet, 2 H), 7.28-7.95 (multiplet, 5 H).

(8 marks)

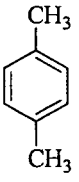
(c) The three xylene (dimethylbenzene) isomers are difficult to distinguish using ^{1}H NMR , but they are easily identifiable by ^{13}C NMR.



o-xylene



m-xylene



p-xylene

(i) Describe how ^{13}C NMR distinguishes these three isomers.

(ii) Explain why they are difficult to distinguish using ^{1}H NMR.

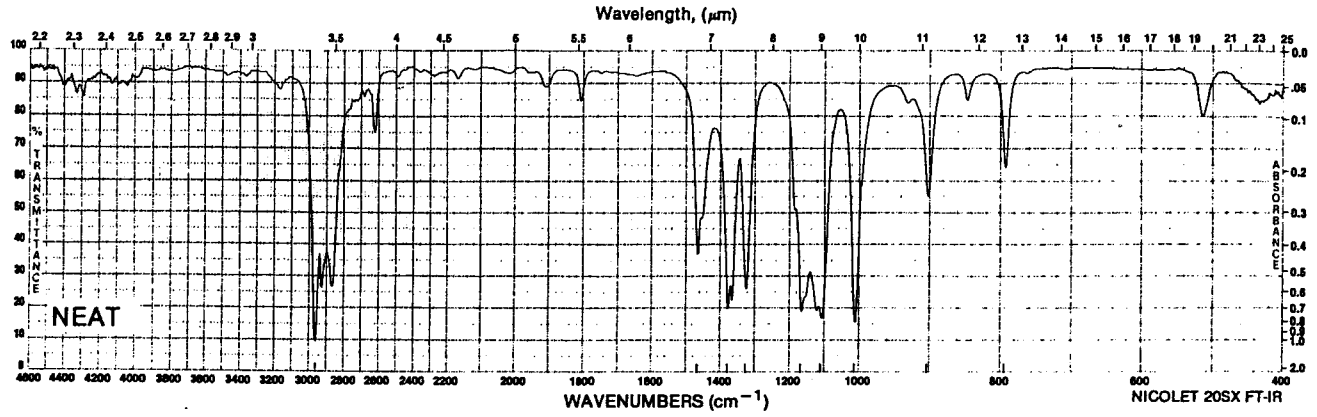
(6 marks)

7. Identify the structure of the compound **9.1** having the spectra below:

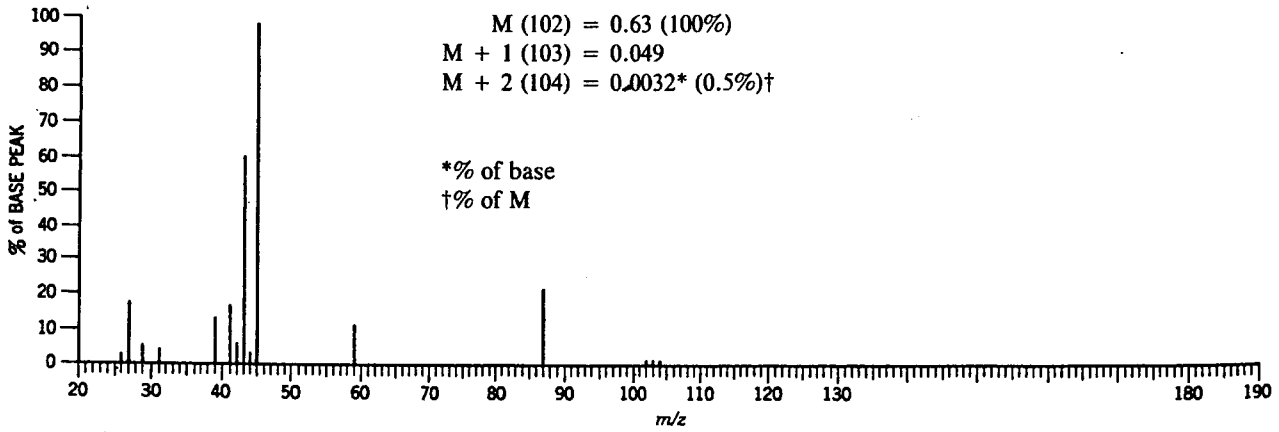
INFRARED SPECTRUM

Compound 9.1

2972.4 1326.9 1015.4
1467.5 1168.9 904.5
1378.8 1111.5 795.5



MASS SPECTRAL DATA (Relative Intensities)



M (102) = 0.63 (100%)
M + 1 (103) = 0.049
M + 2 (104) = 0.0032* (0.5%)†

*% of base
†% of M

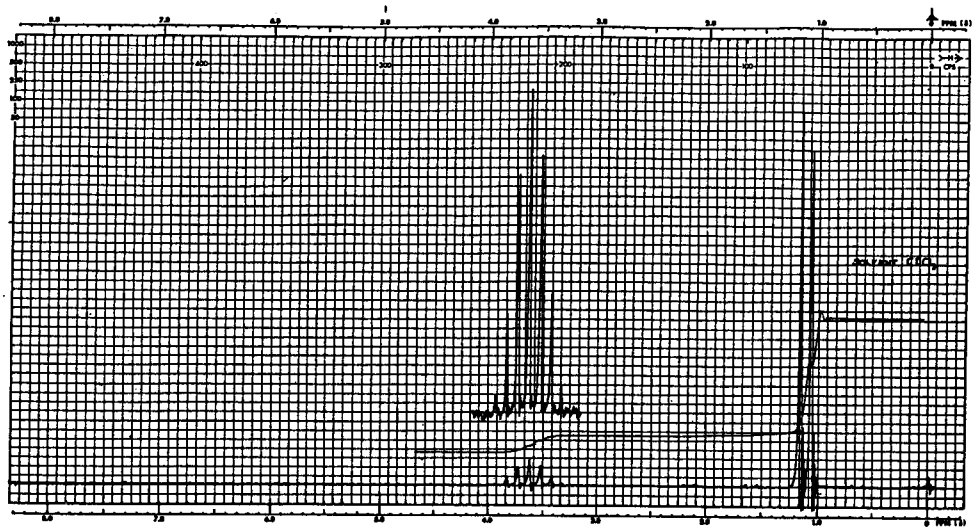
Ultraviolet Data

Transparent above 200 nm

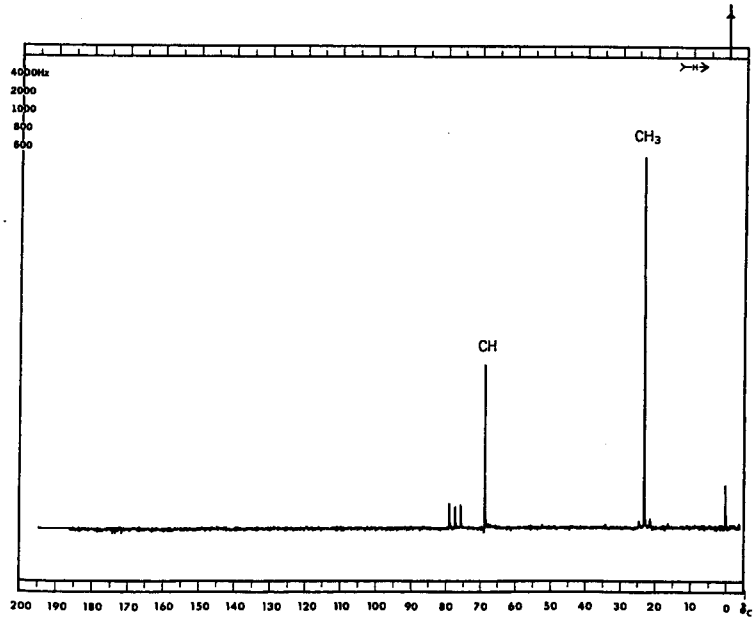
...8/-

Compound 9.1 (continued)

^{1}H NMR SPECTRUM (Solvent $CDCl_3$, 60 MHz)



^{13}C NMR SPECTRUM COMPLETELY DECOUPLED



(20 marks)

TERJEMAHAN

Arahan:

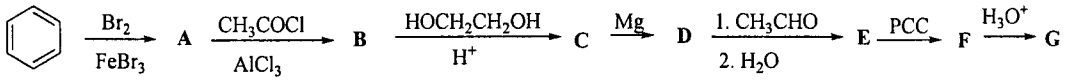
Jawab **LIMA** (5) soalan.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

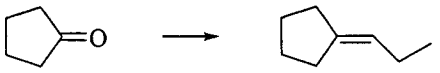
Lampiran: Jadual Spektroskopi.

1. (a) Kenalpasti **A** - **G** dalam urutan tindak balas di bawah. Apabila suatu campuran hasil *orto* dan *para* terbentuk di dalam penukargantian aromatik elektrofilik, pertimbangkan hasil *para* sahaja. Lakarkan spektrum ^{1}H NMR bagi **G**.



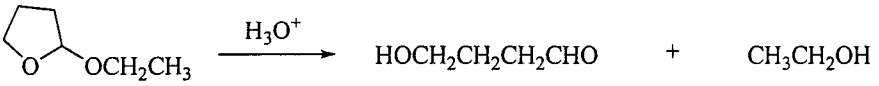
(10 markah)

(b) Tunjukkan dua kaedah yang berbeza untuk melakukan transformasi berikut: suatu kaedah satu-langkah menggunakan reagen Wittig, dan suatu kaedah dua-langkah menggunakan reagen Grignard. Kaedah yang mana satu lebih sesuai bagi transformasi tersebut?



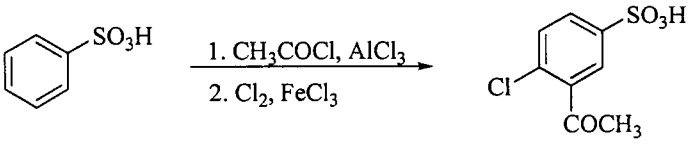
(6 markah)

(c) Tulis suatu mekanisme terperinci bagi tindak balas berikut:



(4 markah)

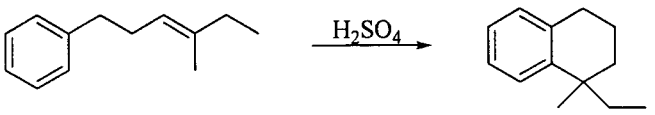
2. (a) Jelaskan kenapa tindak balas berikut tidak memberi hasil **H**. Cadangkan sintesis **H** bermula daripada benzena.



(H)

(6 markah)

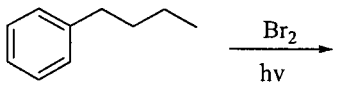
(b) Tulis suatu mekanisme terperinci bagi tindak balas berikut:

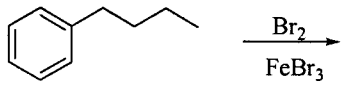


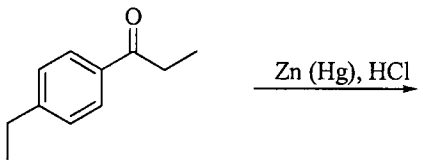
(5 markah)

...11/-

(c) Ramalkan hasil setiap tindak balas berikut:

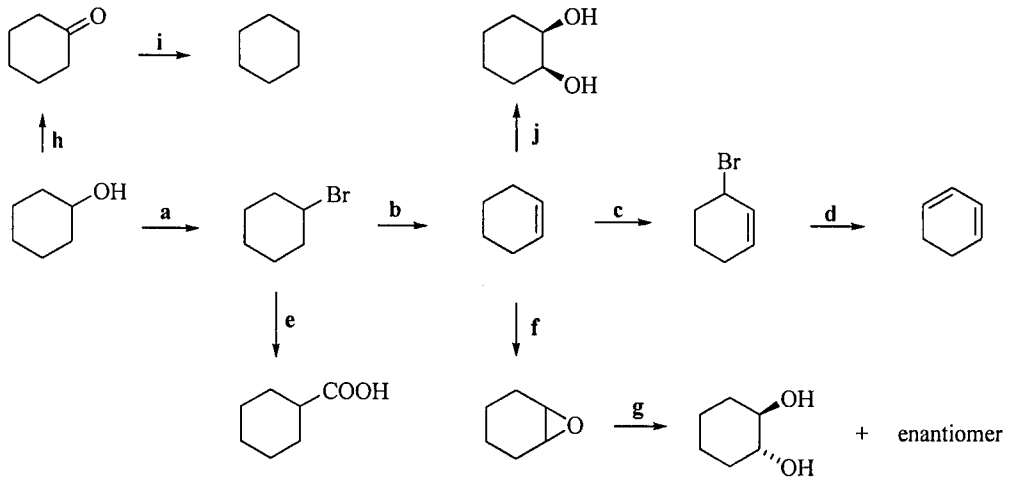
(i) 

(ii) 

(iii) 

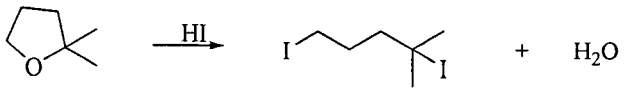
(9 markah)

3. (a) Kenalpasti reagen **a-j** yang diperlukan untuk melakukan setiap tindak balas.



(10 markah)

(b) Tulis suatu mekanisme terperinci bagi setiap tindak balas berikut:

(i) 

(ii) 

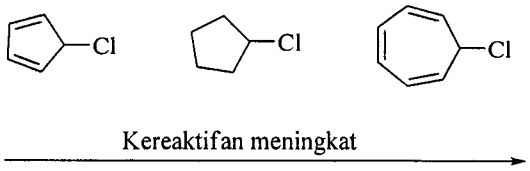
(10 markah)

4 (a) Gunakan peraturan poligon untuk menjelaskan kenapa kation (1) adalah aromatik.

(1)

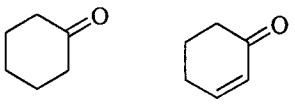
(6 markah)

(b) Jelaskan kadar kereaktifan yang diperhatikan bagi alkil halida 2° berikut di dalam tindak balas S_N1.



(8 markah)

(c) Jelaskan mengapa penyerapan karbonil beranjak ke frekuensi yang lebih rendah dalam suatu sebatian karbonil α, β-tak tepu. Sebagai contoh, penyerapan karbonil kelihatan pada 1720 cm^{-1} bagi sikloheksanon (2), manakala bagi 2-sikloheksenon (3) kelihatan pada 1685 cm^{-1}.



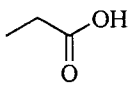
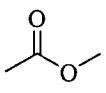
(2) (3)

(6 markah)

5. (a) Bagaimana setiap pasangan sebatian berikut dapat dibezakan menggunakan spektroskopi IR?

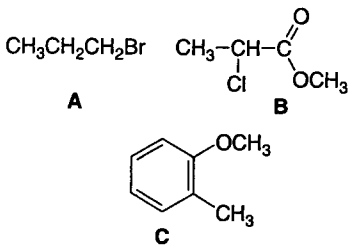
(i)  dan $HC{\equiv}CCH_2CH_2CH_3$

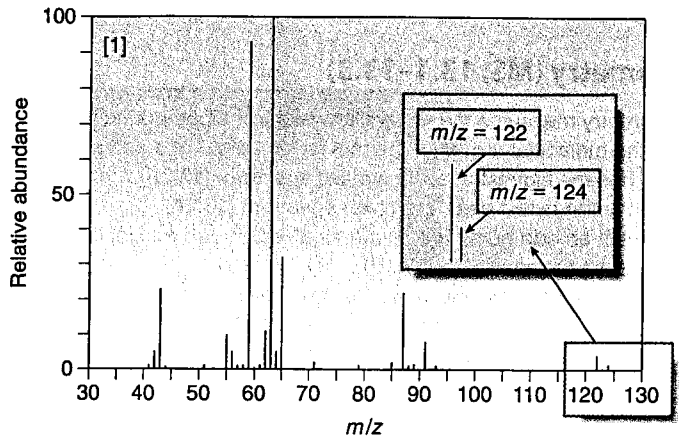
(ii) $HC{\equiv}CCH_2N(CH_2CH_3)_2$ dan $CH_3(CH_2)_5C{\equiv}N$

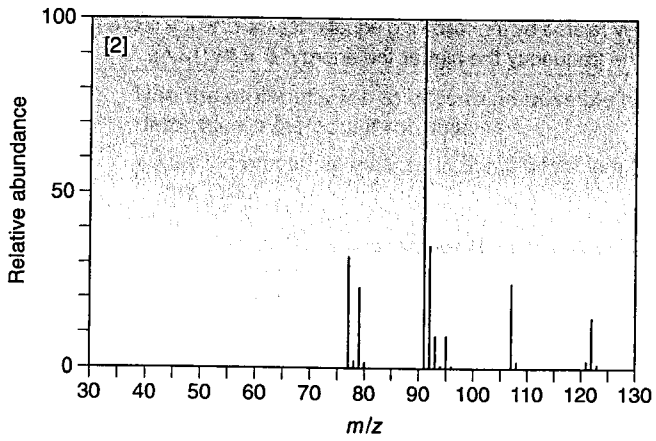
(iii)  dan 

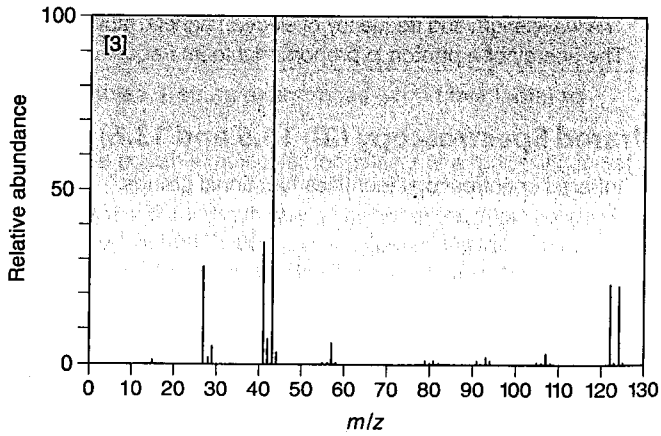
(10 markah)

(b) Spektrum jisim **A, B** dan **C** ditunjukkan di bawah. Padankan setiap struktur dengan spektrum jisimnya.



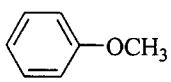
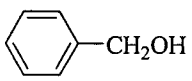






(10 markah)

6. (a) Bagaimana setiap pasangan sebatian berikut dapat dibezakan berdasarkan spektroskopi ^1H NMR?

(i)  dan 

(ii)  dan 

(6 markah)

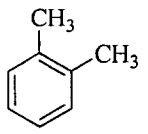
(b) Kenalpasti struktur isomer **I** dan **J**. Sebatian tersebut mempunyai formula molekul $C_9H_{10}O$.

Sebatian **I**: penyerapan IR pada 1742 cm^{-1}; ^1H NMR (ppm): 2.15 (singlet, 3 H), 3.70 (singlet, 3 H), 7.20 (singlet lebar, 5 H).

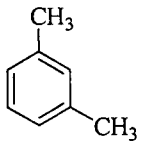
Sebatian **J**: penyerapan IR pada 1688 cm^{-1}; ^1H NMR (ppm): 1.22 (triplet, 3 H), 2.98 (kuartet, 2 H), 7.28-7.95 (multiplet, 5 H).

(8 markah)

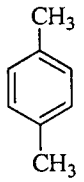
(c) Ketiga-tiga isomer xilena (dimetilbenzena) sukar dibezakan menggunakan ^1H NMR tetapi mudah dikenalpasti dengan ^{13}C NMR.



o-xilena



m-xilena



p-xilena

(i) Tunjukkan bagaimana ^{13}C NMR dapat membezakan ketiga-tiga isomer tersebut.

(ii) Jelaskan mengapa isomer ini sukar dibezakan berdasarkan ^1H NMR.

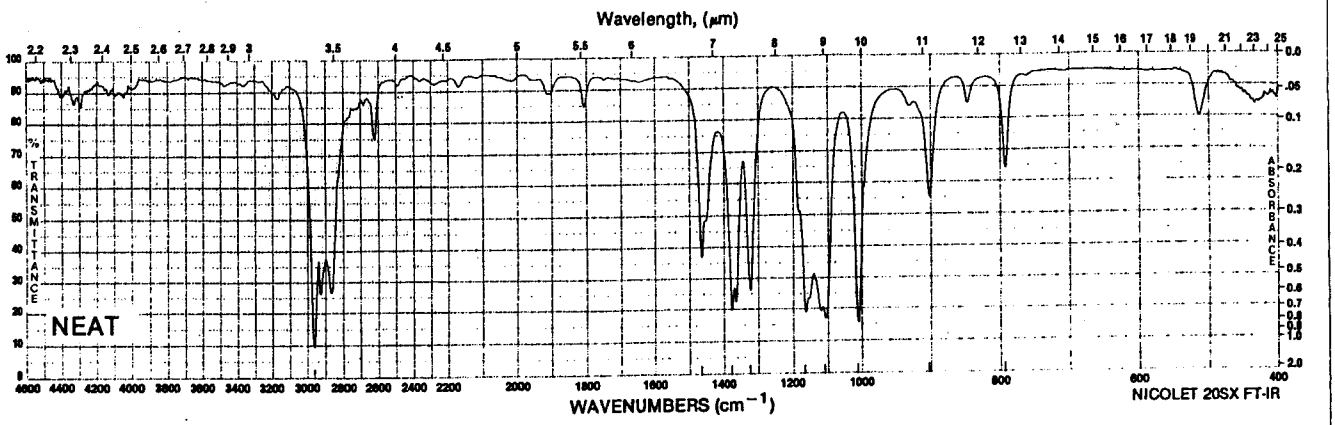
(6 markah)

7. Kenalpasti struktur sebatian **9.1** yang mempunyai spektrum yang ditunjukkan di bawah.

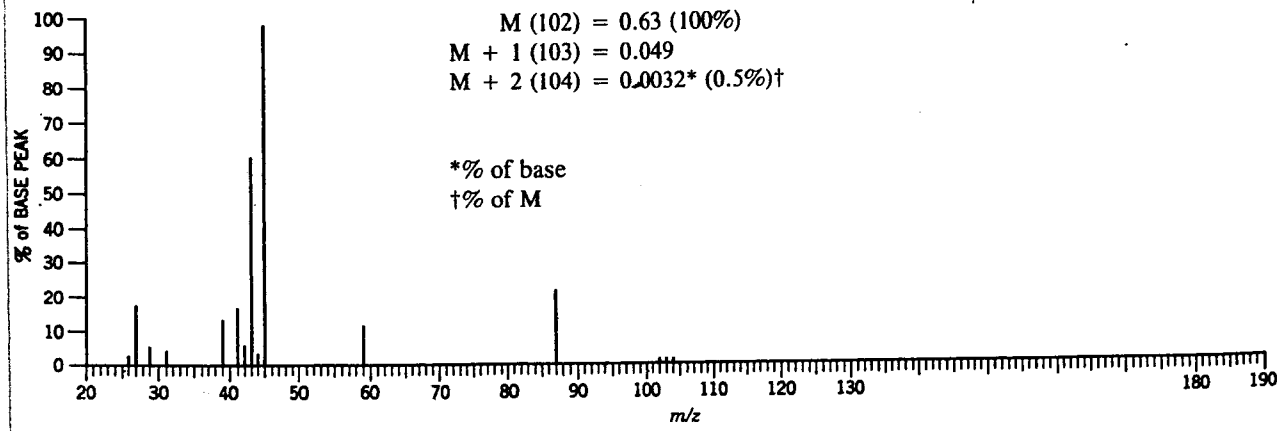
INFRARED SPECTRUM

Compound 9.1

2972.4 1326.9 1015.4
1467.5 1168.9 904.5
1378.8 1111.5 795.5



MASS SPECTRAL DATA (Relative Intensities)



M (102) = 0.63 (100%)
M + 1 (103) = 0.049
M + 2 (104) = 0.0032* (0.5%)†

*% of base
†% of M

Ultraviolet Data

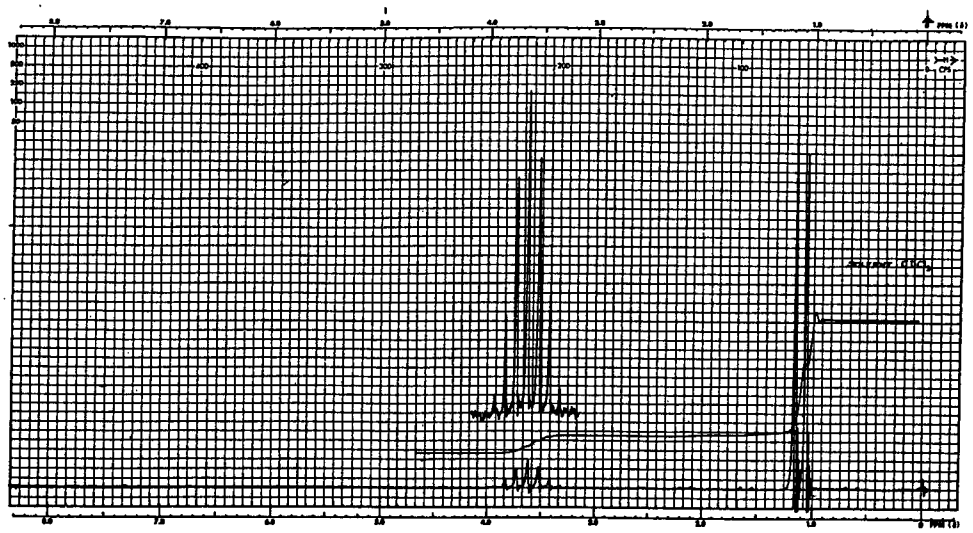
Transparent above 200 nm

(20 markah)

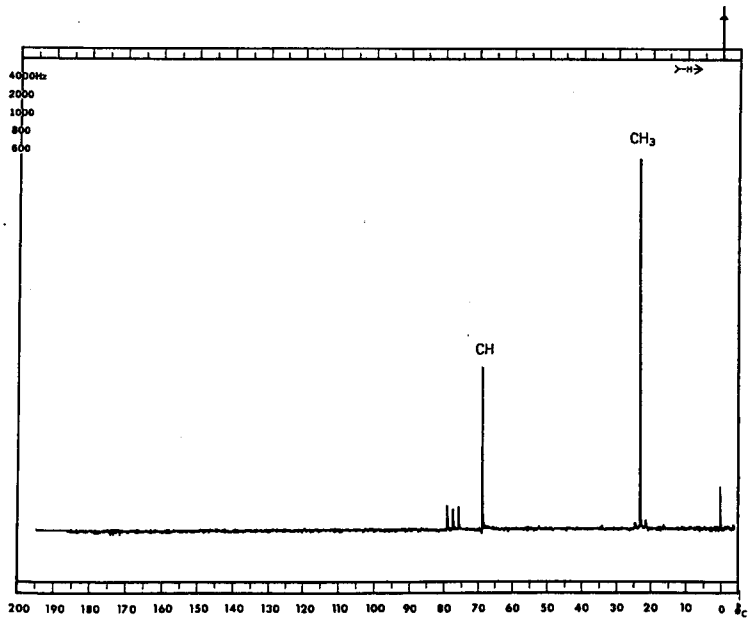
...16/-

Compound 9.1 (continued)

^{1}H NMR SPECTRUM (Solvent $CDCl_3$, 60 MHz)



^{13}C NMR SPECTRUM COMPLETELY DECOUPLED



(20 markah)

Spectroscopy Tables

^{1}H NMR	δ (ppm)
RCH_3	0.9
R_2CH_2	1.3
R_3CH	1.5
C=C-H	4.6-5.9
C ≡ C-H	2.0-3.0
Ar-H	6.0-8.5
Ar - C - H	2.2 -3.0
C=C-CH_3	1.7
H - C - F	4.0-4.5
H-C-Cl	3.0 - 4.0
H - C - Br	2.5-4.0
H - C - I	2.0-4.0
H-C-OH	3.4 -4.0
H - C - OR	3.3-4.0
RCOO - C - H	3.7-4.1
H - C - COOR	2.0 -2.2
H - C - COOH	2.0 -2.6
H-C-C=O	2.0-2.7
R - CHO	9.0-10.0
R-OH	1.0-5.5
Ar-OH	4.0-12.0
C=C-OH	15-17
RCOOH	10.5 - 12.0
RNH_2	1.0 - 5.0

Infrared Absorption	cm^{-1}
= C - H	3020 - 3080
= C - H	675-1000
C = C	1640-1680
≡ C - H	3300
≡ C - H	600-700
C ≡ C	2100-2260
Ar - H	3000-3100
Ar - H	675-870
C = C	1500-1600
O - H	3610 - 3640
O - H	3200 - 3600(broad)
C – O	1080-1300
C = O	1690 - 1760 (s)
O - H (acid)	2500- 3000 (broad)
C - O	1080-1300
C = O	1690-1760
N - H	3300 - 3600
C - N	1180-1360
- NO_2	1515-1560
	1345-1385

^{13}C NMR	δ (ppm)
C – I	0 - 40
C - Br	25 - 65
C-Cl	35 - 80
- CH_3	8 - 30
- CH_2 -	15 - 55
- CH -	20 - 60
≡ C	65 - 85
= C	100 - 150
C - O	40 - 80
C = O	170 - 210
C (Ar)	110 - 160
C - N	30 - 65
C = N	110 - 125

Atomic weight

H = 1.0
C = 12.0
N = 14.0
O = 16.0
F = 19.0
Cl = 35.45
Br = 79.9
I = 126.9
Si = 28.0
P = 31.0
S = 32.0

-oooOooo-